

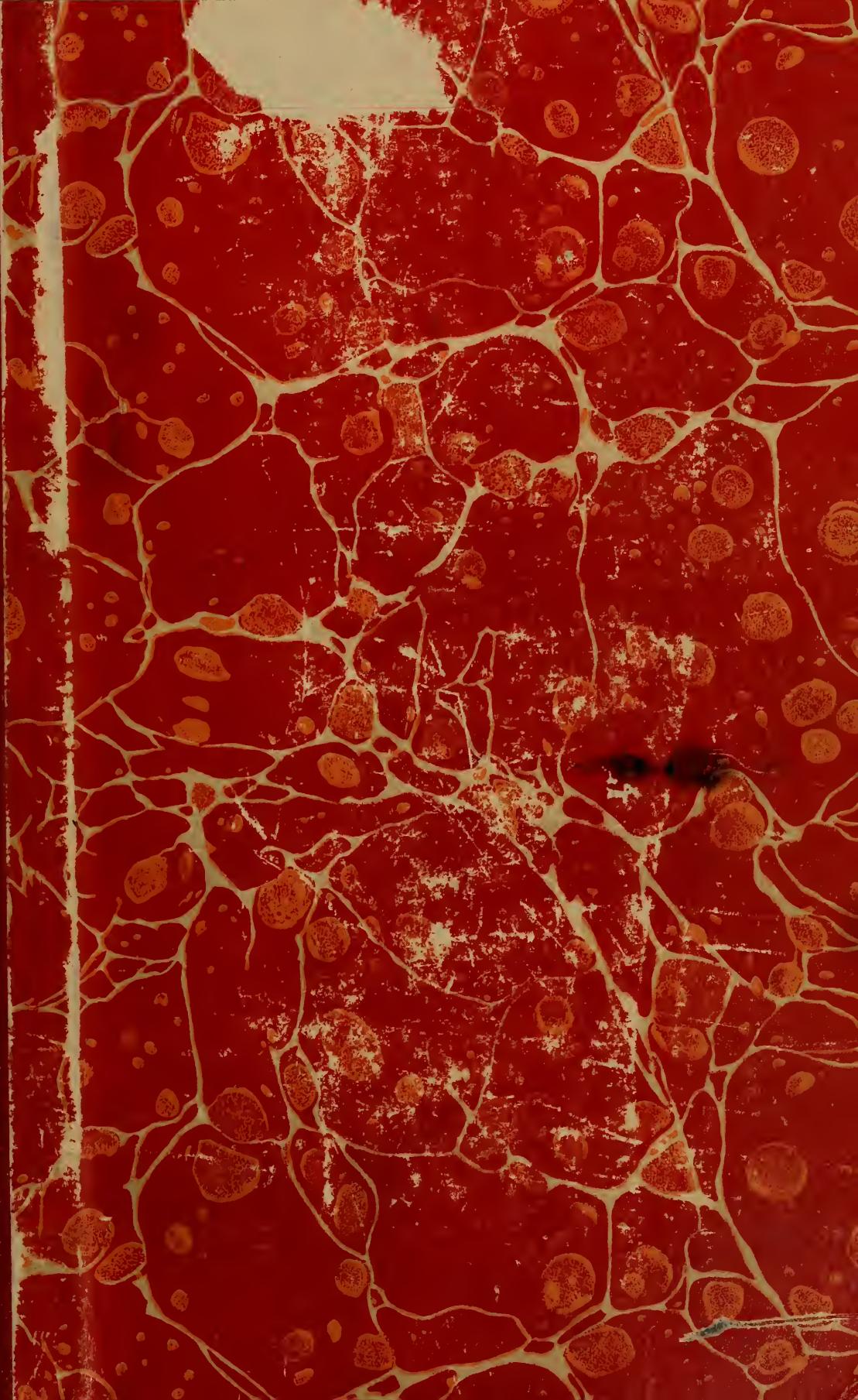
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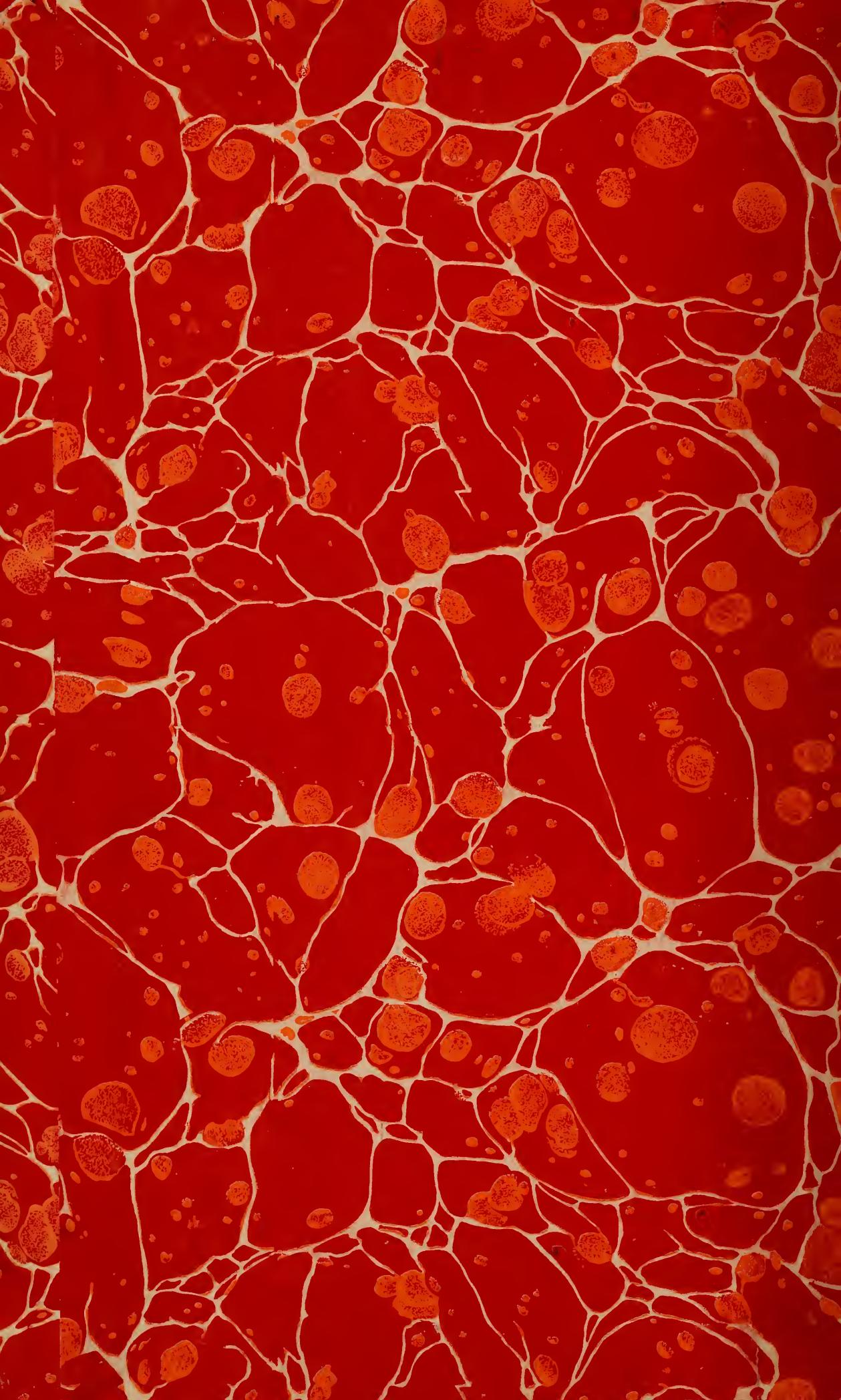
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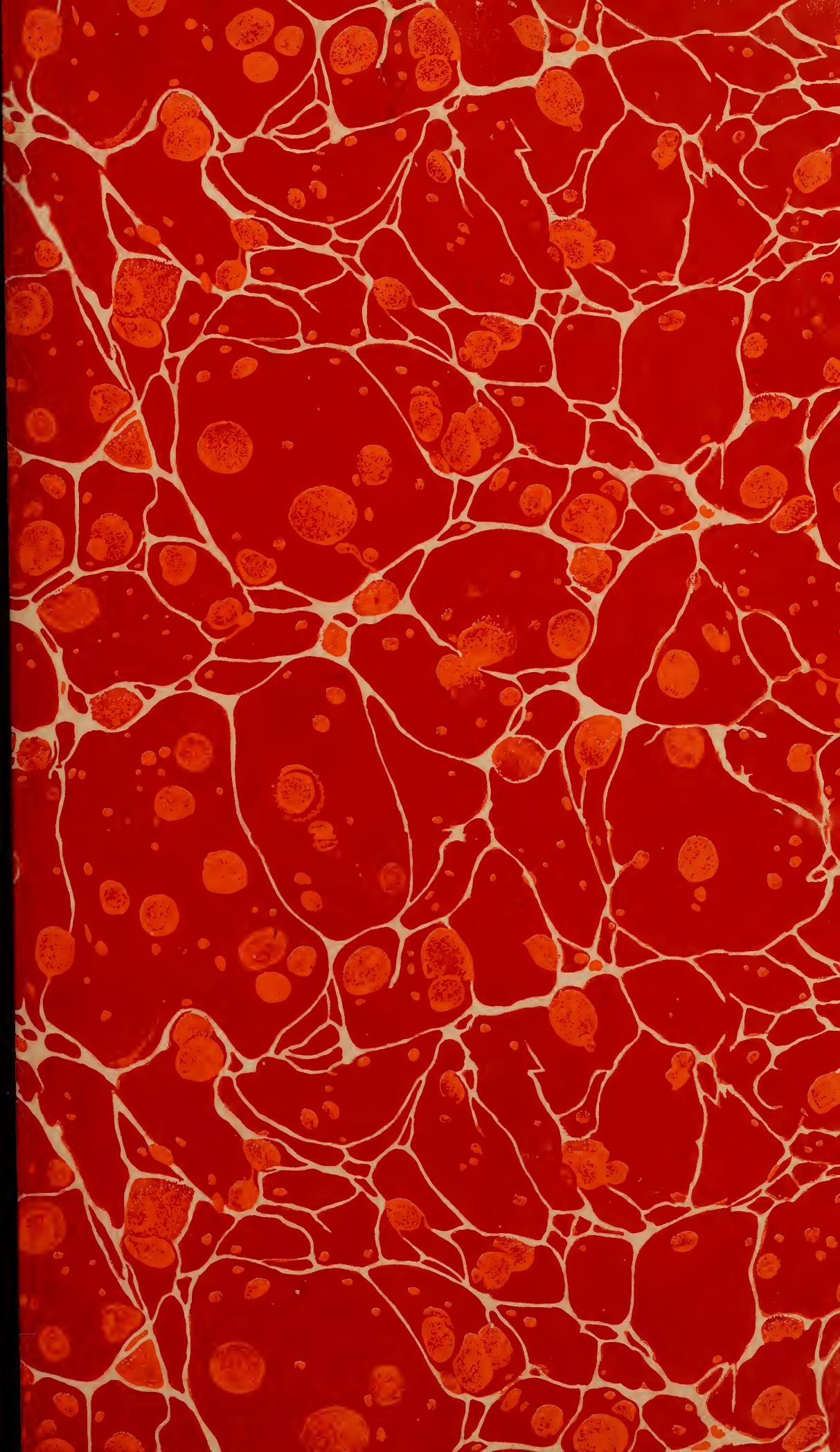


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ISOLATION AND DETERMINATION OF THE CYCLO-HEXANE IN A MIDCONTINENT PETROLEUM¹

By Johannes H. Bruun² and Mildred M. Hicks-Bruun

ABSTRACT

A midcontinent petroleum was fractionated by distillation into a series of 1° cuts. After removal of the benzene from these cuts (by nitration) and subsequent fractional distillation, the cyclohexane was found to concentrate in the fractions boiling at about 80° C. By systematic equilibrium melting it was then possible to isolate the cyclohexane in a state of high purity, 99.96 mole per cent. The following physical constants were determined for the isolated cyclohexane: Boiling point, freezing point, specific gravity, refractive index, molecular weight, and the critical solution temperature with aniline. Photographs were also taken of the visible and ultra-violet, as well as the infra-red, absorption spectrum of the isolated hydrocarbon.

The petroleum fraction with boiling range of 80° to 80.5° C. was found to consist of about 94 mole per cent of cyclohexane. Based upon the crude petroleum, the percentage of cyclohexane was found to be about 0.33.

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I. INTRODUCTION

A short time after cyclohexane had been synthesized by Baeyer,³ Markownikoff⁴ was able to show that Caucasian petroleum fractions boiling around 80° C. consisted mainly of this naphthene. Although the presence of cyclohexane has been indicated in many other crude petroleums since that time, it seems that only two investigators have been able to isolate it in a demonstrably pure condition. Chavanne⁵ isolated a sample of cyclohexane, the freezing point of which was +3.2° C. (the freezing point of pure synthetic cyclohexane is +6.4° C.) and Fortey⁶ obtained a cyclohexane sample with a freezing point of +4.7° C. In addition to physical methods, such as distillation and fractional melting, however, Fortey also subjected the

¹ This paper describes some of the results obtained in an investigation on the separation, identification and determination of the chemical constituents of commercial petroleum fractions listed as Project No. 6 of the American Petroleum Institute research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by John D. Rockefeller. This fund is being administered by the institute with the cooperation of the Central Petroleum Committee of the National Research Council.

² Research associate for the American Petroleum Institute.

³ A. Baeyer, Ann., 278, p. 111; 1894.

⁴ W. Markownikoff, Ber., 28, p. 577; 1895; 30, p. 974; 1897.

⁵ G. Chavanne, J. soc. chim. Belg., 31, p. 361; 1922.

⁶ E. C. Fortey, J. Chem. Soc., 73, p. 932; 1898; 75, p. 873; 1899.

fractions to the destructive action of chlorosulphonic acid, a procedure which we have avoided since it would render impossible the identification of the other hydrocarbons in these petroleum fractions.

II. ORIGIN AND PRELIMINARY DISTILLATION OF THE CRUDE PETROLEUM

The crude petroleum used for this investigation was obtained from No. 6 well of the South Ponca Field, Kay County, Okla.⁷ The preliminary distillation of the crude oil was carried out in a semicommercial batch still⁸ capable of handling a charge of 200 gallons. This still was provided with a rectifying column which consisted of 20 bubbling cap plates. Three charges of 200 gallons each were made

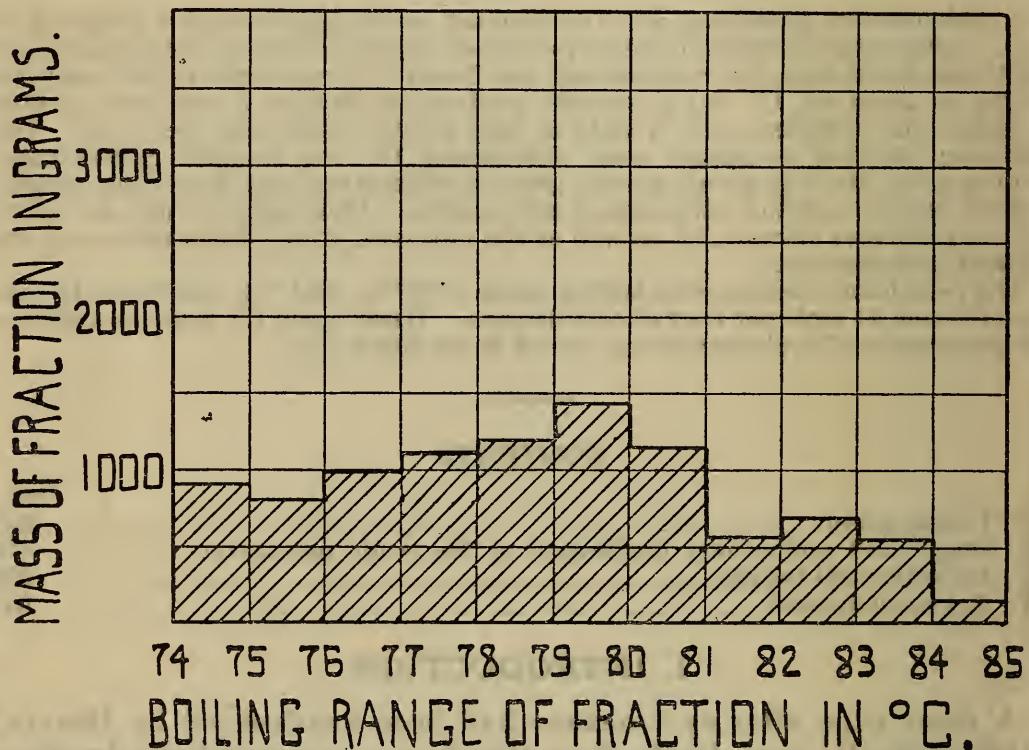


FIGURE 1.—Distribution of the fractions over their boiling range before removal of the benzene

in this still, and the corresponding fractions from these distillations were blended into 4-gallon cuts, which were sent to the bureau.

These fractions were redistilled in the stills previously described,⁹ with the further assistance of an all-glass still, which has a 35-foot column, packed with chromium plated steel jack chain. In all of the glass stills the rate of distillation was maintained at about 1 ml per minute and a reflux ratio of 10:1 was used. The boiling points of the fractions were determined accurately by means of the continuous boiling point apparatus previously described.¹⁰ Each boiling point was corrected to standard pressure.

As a result of these preliminary distillations the material was fractionated into a series of 1° cuts. The present investigation deals with the fractions between 74° and 85° C.

⁷ For properties see E. W. Washburn, J. H. Bruun, and M. M. Hicks, B. S. Jour. Research, 2, p. 469 Table 1; 1929.

⁸ Acknowledgment for this distillation is made to A. E. Pew, Jr., and R. B. Davidson, of the Sun Oil Co.

⁹ J. H. Bruun and M. M. Hicks-Bruun, B. S. Jour. Research, 6, p. 870; 1931.

¹⁰ See footnote 9.

III. EXPERIMENTAL RESULTS

The graph in Figure 1 shows the distribution of the petroleum fractions over the boiling range after completion of the preliminary distillations. From this graph it will be noted that 1,200 g of material had a boiling range of 80° to 81° C. (the boiling points of cyclohexane and of benzene are 80.8° and 80.2° C., respectively). For the purpose of removing and determining the benzene, each of the cuts with boiling ranges between 74° and 85° C. was subjected to nitrating treatment according to the method described in previous papers.^{11, 12}

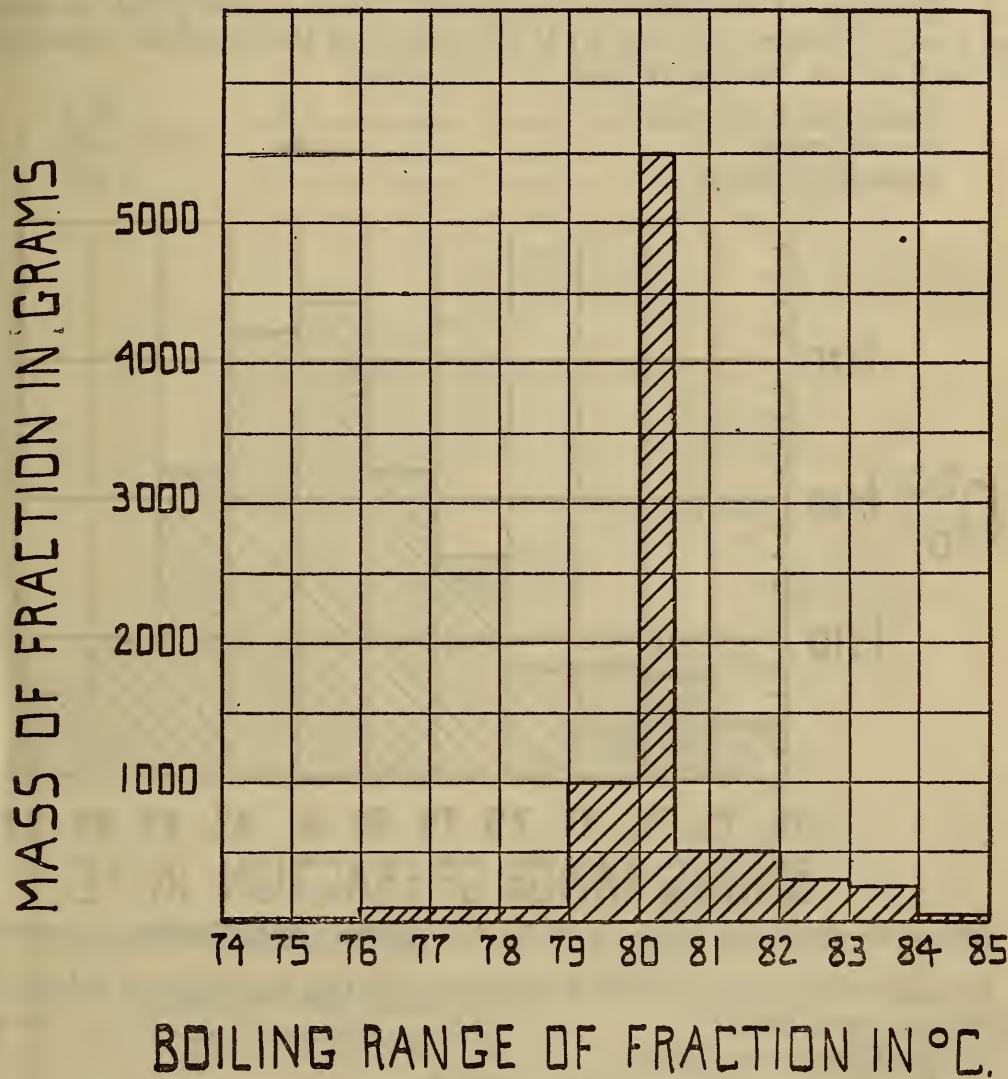


FIGURE 2.—Distribution of the fractions over their boiling range after removal of the benzene and subsequent fractional distillations

After the nitration the remaining hydrocarbons were washed with sodium-hydroxide solution and with distilled water, and finally dried over calcium chloride.

When the benzene had been completely removed the aromatic-free fractions were subjected to five more distillations. All of these distillations, as well as the last three of the preliminary distillations, were

¹¹ J. H. Bruun and M. M. Hicks-Bruun, B. S. Jour. Research, 6, pp. 869-880; 1931.

¹² J. H. Bruun, R. T. Leslie, and S. T. Shicktanz, B. S. Jour. Research, 6, pp. 767-768; 1931.

made by S. T. Shicktanz and a staff of still operators. During these distillations most of the material concentrated in the cut boiling between 80° and 80.5° C. The distribution of the fractions over their boiling range at this stage of the investigation is shown in Figure 2.

Figure 3 shows the refractive indices of the different fractions plotted against the boiling range. The maximum on this graph exhibited by the fractions boiling between 80° and 81° C., and the high freezing points of these fractions were taken as indications of the presence of cyclohexane.

At this stage of the investigation about 7 liters (5,500 g) of material had a boiling range of 80° to 80.5° C. Some of the physical properties of this fraction were as follows:

Boiling point (corrected)	° C	80.4
Freezing range	do	-12 to -36
Refractive index ²⁰		1.422

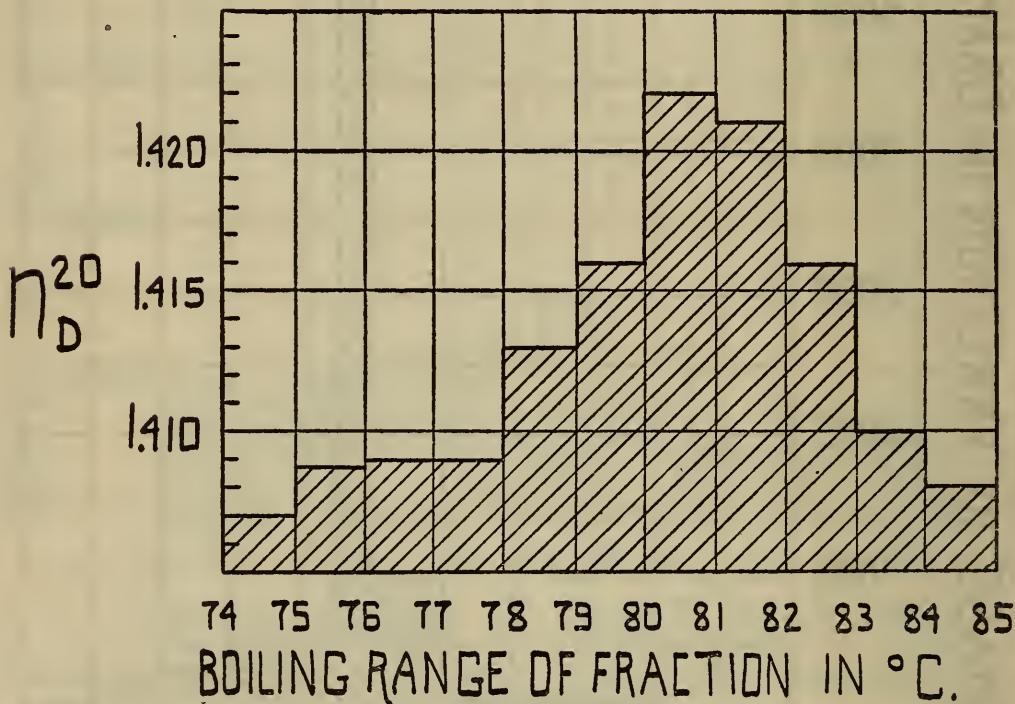


FIGURE 3.—Refractive indices of the fractions plotted against their boiling range

In order to separate the cyclohexane from this mixture the following methods were tried:

1. Equilibrium melting.
2. Distillation with methyl alcohol.¹³
3. Distillation with ethyl alcohol.¹³
4. Distillation with aniline.
5. Extraction with aniline.¹⁴
6. Extraction with benzyl alcohol.¹⁵

As the first of these six methods gave by far the sharpest separation, a systematic fractionation of the material by means of equilibrium melting was undertaken. The method and technic used depended upon the freezing ranges of the fraction and the quantities of material available. The first fractionations of the comparatively large fractions

¹³ For details see J. H. Bruun and M. M. Hicks-Bruun, *B. S. Jour. Research*, **5**, pp. 933-942; 1930.

¹⁴ For details see footnote 11, p. 609.

¹⁵ For details see H. Steinbrecher, *Braunkohlenarchiv*, Heft, **31**, p. 1; 1930.

(with freezing ranges of -30 to -10) were made in a closed apparatus.¹⁶ For the resulting smaller fractions with higher melting points it was found more convenient to use a vacuum funnel.¹⁷

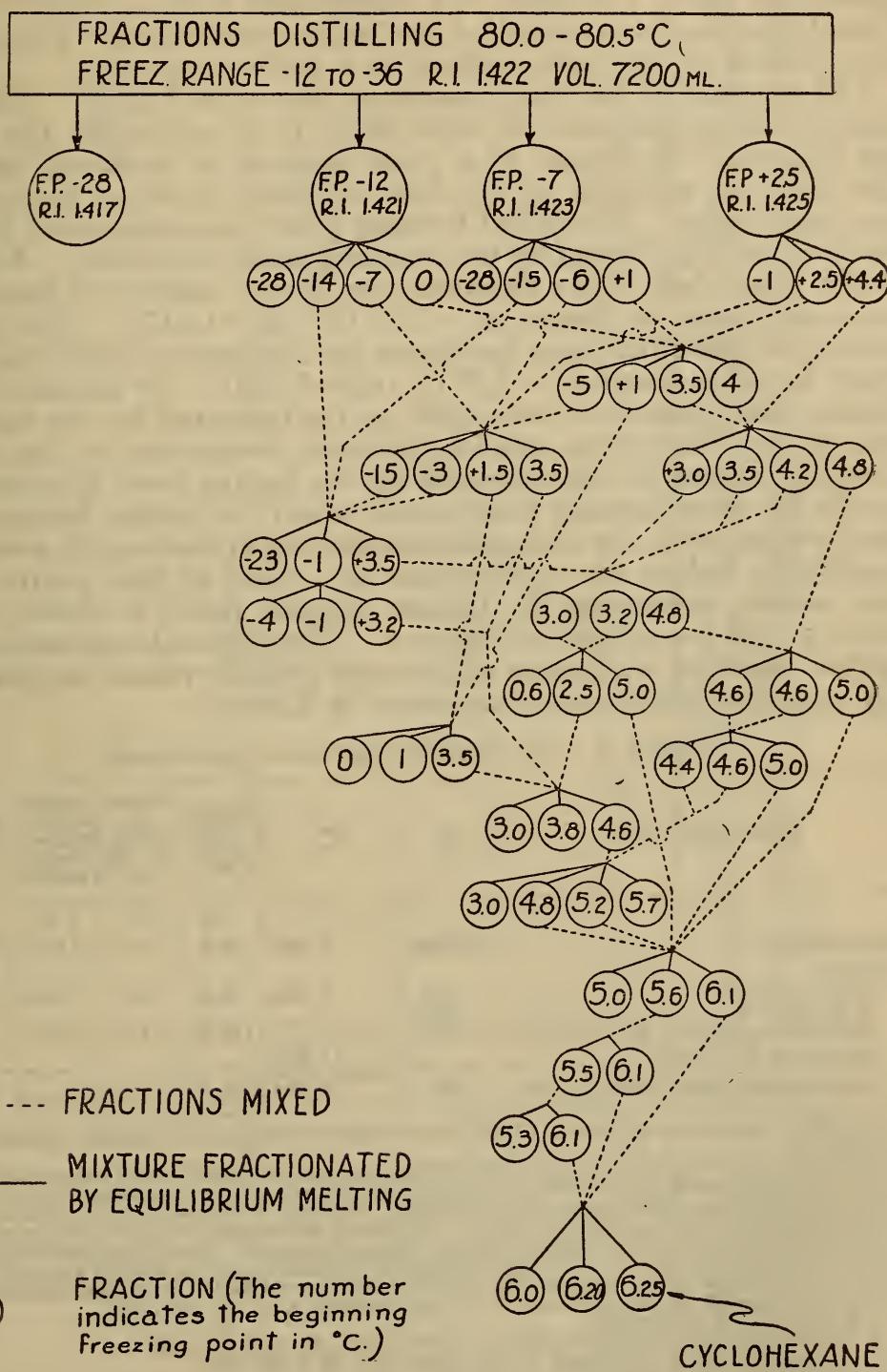


FIGURE 4.—Chart showing the isolation of the cyclohexane by equilibrium melting

However, as soon as fractions with freezing ranges above 0° C . were obtained, an ordinary Büchner funnel (covered with a watch glass) was used instead of the vacuum funnels. Suction was applied

¹⁶ R. T. Leslie and S. T. Schicktanz, B. S. Jour. Research, 6, p. 382; 1931.

¹⁷ For details see M. M. Hicks, B. S. Jour. Research, 2, p. 484; 1929.

from below, and the unmelted crystals were pressed "dry" by means of a spatula.

For the final crystallization the material was placed in a bottle and allowed to stand overnight in a refrigerator kept at about $+3^{\circ}$ C. After 18 hours about one-half of the fraction was frozen. The crystals were filtered off and recrystallized in a similar manner.

The progress of the fractionation is shown in Fig. 4.¹⁸ The large fraction boiling between 80° and 80.5° C. is shown at the top of the diagram. By means of a great number of fractional meltings, this large cut was split up into four different fractions, indicated by the large circles. The initial freezing point was determined for each fraction and is indicated by the numbers inside the circles. As shown at the upper left of the diagram, the lowest melting of these large fractions began to freeze at -28° C. ($n_D^{20} = 1.417$). The highest melting of these fractions (as shown by the large circle at the upper right) began to freeze at $+2.5^{\circ}$ C. ($n_D^{20} = 1.425$). By further crystallization these fractions were split up (as indicated by the unbroken lines in the chart) into smaller fractions, designated by the smaller circles in Figure 4. As indicated by the broken lines, fractions with nearly the same freezing points were mixed for further fractionation. By the systematic use of equilibrium melting in this way, it was finally possible to isolate the cyclohexane in a state of high purity. The final sample, possessing the highest freezing point, is shown by the arrow at the lower right in Figure 4. The physical constants of this sample, together with some of the most reliable values for synthetically prepared cyclohexane, are given in Table 1:

TABLE 1.—*The physical constants of cyclohexane*

Cyclohexane, C ₆ H ₁₂	d_4^{20}	n_D^{20}	Boiling point corrected	Freezing point (in dry air)	Critical solution temperature in aniline	Molecular weight
From petroleum.....	1 0.77849	1.4263	80.8° C.	6.25° C.	$^{23} 31.0^{\circ}$ C.	$^{13} 83.9 \pm 0.2$ 84.0 ± 0.2
Synthetic:						
J. Timmermans ⁴7785	1.4263	80.8° C.	6.4° C.	31.0	—
F. Eisenlohr ⁵7783	—	—	—	—	—
Beilstein Ergänzungsl. 5, p. 6; 1930.....	6.7791	—	7 80.75	6.4	31.0	—
Beilstein 5, p. 21; 1922.....	—	{ 1.4266 (at 19.5° C.) }	—	—	—	—
International Critical Tables 1, p. 202.....	.779	1.4272	81.4	6.5	—	84.09

¹ ± 0.00001 . Determined by Miss E. E. Hill, of the division of weights and measures, National Bureau of Standards.

² Known amounts of cyclohexane and freshly distilled dry aniline, with a boiling range of 0.1° C., were placed in a double-walled tube, which was equipped with a stirrer, a thermometer (accurate to 0.1° C.) and suitable protection against atmospheric moisture. This tube was heated in a petrolatum bath, the temperature of which was carefully controlled. The critical temperature of solution was determined by slowly raising as well as slowly lowering the temperature of the bath. The values observed by heating and cooling checked to 0.1° C. The weight per cent of hydrocarbon in the mixture was varied from 50 to 75 per cent, and the critical temperature of solution was observed for the 60 per cent composition.

³ For method see M. M. Hicks-Bruun, B. S. Jour. Research, 5, pp. 575-583; 1930.

⁴ J. chim. phys., 23, p. 760; 1926.

⁵ F. Eisenlohr, Fortschritte Chem. Physic, physik. Chem., 18, pt. 9, p. 1; 1925.

⁶ T. W. Richards and J. W. Shipley, J. Am. Chem. Soc., 38, p. 996; 1916.

⁷ J. Timmermans, Chem. Zentr., 82, p. 1669; 1911.

⁸ G. Chavanne and L. J. Simon, Compt. rend., 168, p. 1112; 1919.

⁹ N. Zelinsky Ber., 34, p. 2802; 1901.

The visible and ultra-violet absorption spectra of the vapor were determined by M. Davis, of this bureau, at pressures ranging from about 1 to 48 mm. No absorption lines or bands were observed in the region $\lambda = 2,300$ to $4,878$ Å.

¹⁸ Acknowledgment is made to F. W. Rose, jr., for drawing the chart in Figure 4.

Figure 5 is the infra-red absorption spectrum of the liquid. This work was done by U. Liddel, of the Fixed Nitrogen Research Laboratory, Department of Agriculture.

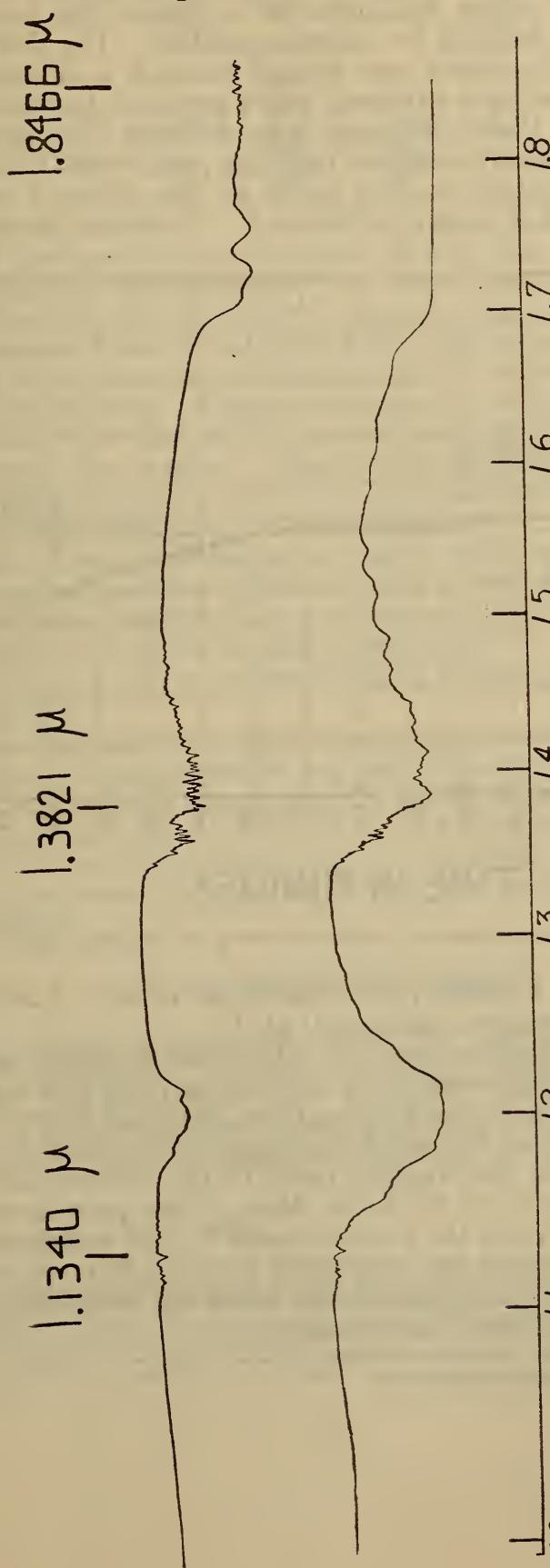


FIG. 5.—*Infra-red absorption spectra of 1 mm and 1 cm cells, respectively, of the isolated cyclohexane.* Slit width approximately 10 A.
These are automatically registered energy curves of the emission from a tungsten filament (approximately 2,900° C.) through the cells containing the cyclohexane. Calibration was made on the basis of the Hg lines in this region from the published data on their wave lengths. The wave lengths of the H₂O lines, read from this calibration, curve check the published wave lengths of H₂O within ± 2 A. The two absorption maxima occurring at 1.72μ and 1.206μ are the first and second overtones, respectively, of the fundamental H to C vibration occurring at approximately 3.4μ observed in all hydrocarbon compounds. The band at 1.42μ is a combination band of this fundamental with another near 6μ . Measured by U. Liddel, of the Fixed Nitrogen Research Laboratory, Department of Agriculture.

As shown in Table 1, there is excellent agreement between the physical constants of the isolated hydrocarbon and those of the pure cyclohexane, prepared synthetically. Although in this case the physical constants alone are sufficient evidence for identification, further proof was obtained by dehydrogenation. For this purpose a sample of the hydrocarbon was passed through a dehydrogenation furnace (using nickel as a catalyst) and a product, the odor of which strongly resembled that of benzene, was obtained. By nitration this product yielded *m*-dinitrobenzene (melting point = 89.7° C.).

The time-temperature cooling curve of the isolated cyclohexane was determined and is shown in Figure 6. Duplicate determinations

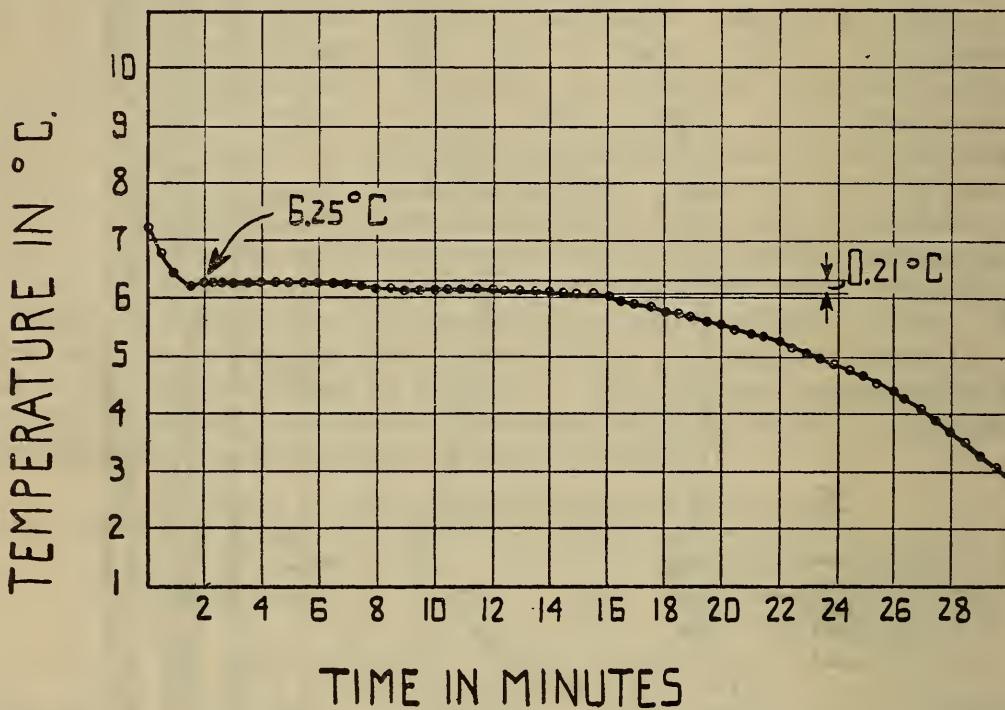


FIGURE 6.—Time-temperature cooling curve of the isolated cyclohexane

were made and the freezing point was found to be +6.25° C. The whole sample froze within a range of 0.21° C.

The purity of the cyclohexane was determined by direct comparison (with a Beckmann thermometer) of its freezing point and the freezing point of a pure sample of this hydrocarbon, obtained from the Bureau International d'Etalons Physico-Chimiques (in Brussels). According to this determination the freezing point of the cyclohexane isolated from petroleum was 0.13° C. below that of the pure hydrocarbon. From this value and from the heat of fusion ¹⁹ (5.87 calories per gram) of cyclohexane the purity was calculated to be 99.96 mole per cent.

As a result of this investigation the following quantities of cyclohexane were isolated from the petroleum:

¹⁹ M. Padua, Atti Accad. Lincei, 28, p. 240; 1919.

TABLE 2.—Quantities of cyclohexane isolated from the petroleum

Approximate volume	Initial freezing point (in air)	Purity	Approximate volume	Initial freezing point (in air)	Purity
ml	° C.	Mole per cent	ml	° C.	Mole per cent
200	6.25	99.96	600	5.7	99.77
200	6.2	99.94	700	3.0	98.88
200	6.1	99.91	1,400	+1	98.22
500	6.0	99.88	1,000	-7	95.58

Figure 2 displays the approximate distribution of the cyclohexane in the petroleum fractions used for this investigation. From the beginning freezing point, -12° C. (see the top of fig. 4) of the 80° to 80.5° fraction it can be calculated that this large fraction contained about 93.7 mole per cent of cyclohexane^{20 21} before it was subjected to equilibrium melting. From a conservative estimate of the fractions boiling between 74° and 85° C. we can conclude that at least 6,700 g of cyclohexane was present. Based upon the original 600 gallons of crude oil (specific gravity 0.90), the cyclohexane content is found to be about 0.33 per cent.

As to the possible utilization of the cyclohexane in petroleum, it should be noted that this hydrocarbon is a very desirable solvent for molecular weight determinations in chemical laboratories. Its main advantages over benzene for this purpose are:

1. Cyclohexane has an unusually high cryoscopic constant, 20° C. per mole per kg.
2. Being a naphthalene hydrocarbon, its properties are intermediate between those of the aromatic and the aliphatic hydrocarbons. For this reason it should be more generally useful than benzene.

The minor constituents of the fractions boiling between 74° and 85° C. were found to consist mainly of 2, 2-dimethylpentane. The isolation of this hydrocarbon is in progress and the results will be published in a later paper.

IV. ACKNOWLEDGMENT

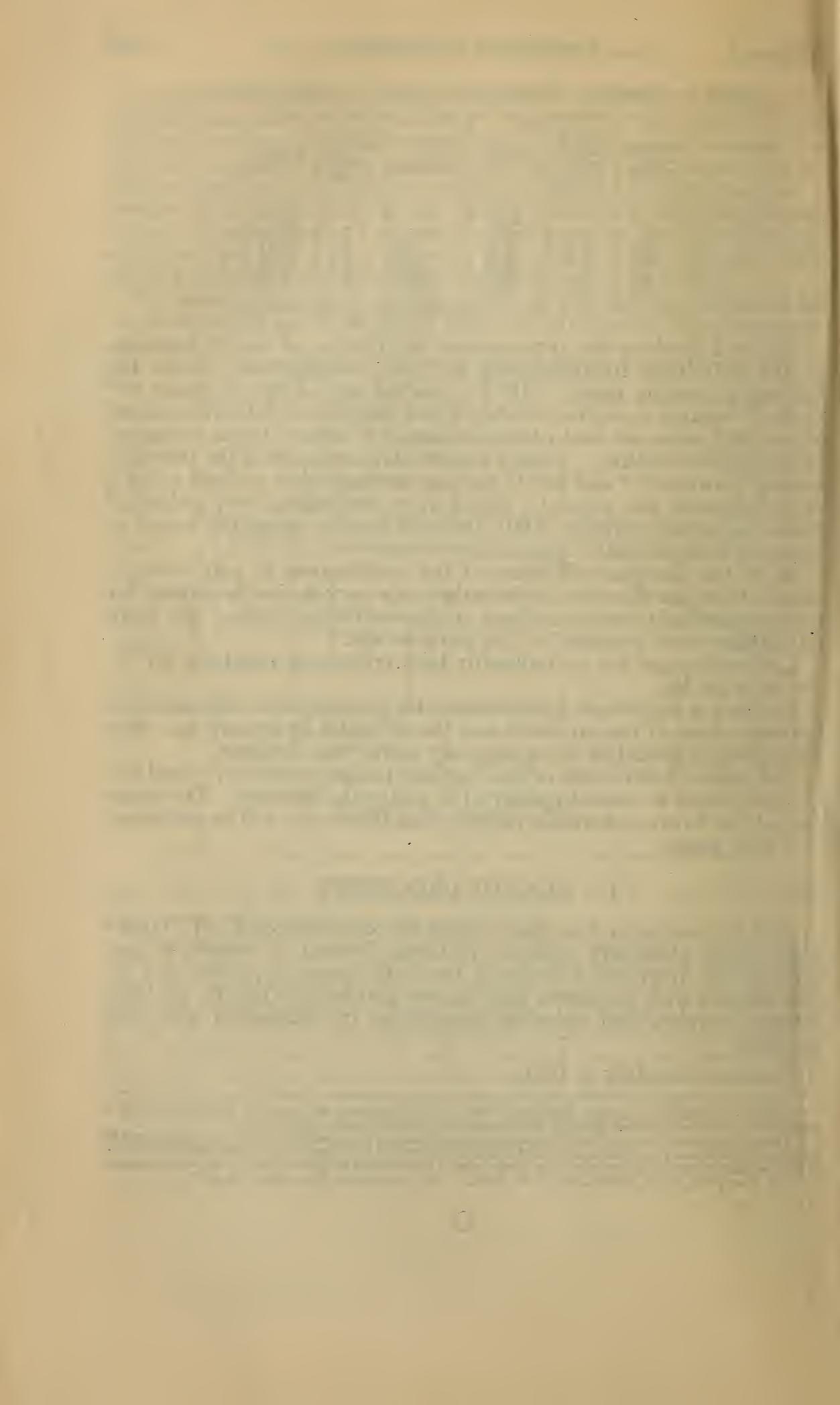
This investigation was made under the direction of E. W. Washburn, chief, chemistry division, National Bureau of Standards and director of American Petroleum Institute research project No. 6. The authors wish to express their sincere gratitude to him for his kind interest, advice, and valuable suggestions in connection with the problem.

WASHINGTON, July 6, 1931.

²⁰ Because benzene has a greater antiknock effect than cyclohexane, the value of this fraction, for a motor fuel, could be improved upon by dehydrogenating the cyclohexane to benzene.

²¹ This investigation indicates that the separation of cyclohexane from petroleum on an industrial scale is feasible. This fact may prove to be of interest if cyclohexane would be accepted as an upper reference standard for antiknock tests of motor fuels. The advantages of cyclohexane for this purpose have been discussed by J. M. Campbell, W. G. Lowell, and T. A. Boyd, J. Soc. Automotive Eng., 26, p. 163; 1930.





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